EUROPEAN PATENT SPECIFICATION

(54) **Method of and device for determining spectrum parameters of a spectrum related to spectroscopic signals.**

(73) Proprietor: **N.V. Philips' Gloeilampenfabrieken**
Groenewoudseweg 1
NL-5621 BA Eindhoven(NL)

(72) Inventor: **Van Ormondt, Dirk**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven(NL)
Inventor: **De Beer, Ronald**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven(NL)

(74) Representative: **Zwaan, Andries Willem et al**
INTERNATIONAAL OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)

Description

The invention relates to a method of determining spectrum parameters of a spectrum in a frequency domain, related to spectroscopic signals in the time domain, in which method the spectroscopic signals derived from a substance are sampled in order to obtain sampling values and are approximated by a complex model function which contains the spectrum parameters and exponentially damped sinusoids, in which method there is also made an initial estimate, based on the sampling values, for the spectrum parameters occurring non-linearly in the model function, the spectrum parameters being accurately estimated from the model function by iteration with a least-squares optimisation procedure, and prior knowledge is introduced into the model function.

The invention also relates to a device for determining spectrum parameters of a spectrum in a frequency domain, related to spectroscopic signals in the time domain, which device comprises means, for generating the spectroscopic signals in a substance, sampling means for obtaining sampling values from the spectroscopic signals, and display means for displaying the spectrum, and also comprises programmed means which comprise a complex model function containing the spectrum parameters and exponentially damped sinusoids, and are suitable for storing prior knowledge of the spectroscopic signals as well as for making an initial estimate for the spectrum parameters occurring non-linearly in the model function and for executing a least-squares optimisation procedure for the model function on the basis of the sampling values, the programmed means furthermore comprising iteration means for accurately estimating, using iteration, the spectrum parameters by means of the least-squares optimisation procedure.

A method of this kind is inter alia suitable for signals which are mainly exponentially damped, for example for signals obtained during a magnetic resonance experiment from an entire body as the substance as well as from a part of the body. The method can also be used, for example for X-ray spectroscopy or FT infrared spectroscopy.

A method of this kind is disclosed in an article by J.W.C. van der Veen et al, "Accurate Quantification of in Vivo ^{31}P NMR Signals Using the Variable Projection Method and Prior Knowledge", Magnetic Resonance in Medicine, Vol. 6, No. 1, January 1988, pp.92-98.

The spectrum parameters of a spectrum related to spectroscopic signals (signals obtained during an NMR experiment) are derived via the sampling values (represented in a time domain, which is in contrast with the spectrum which is represented in a frequency domain), directly in the time domain. A least-squares optimisation procedure is used for fitting the sampling values to a model function of spectroscopic signals, in which procedure prior knowledge concerning spectral components can be introduced. The method can in principle be used for an arbitrary model function. In said article, for example a model function is assumed which contains exponentially damped sinusoids. By operation in the time domain, arbitrary parts of the spectroscopic signals can be omitted without giving rise to serious fitting problems. For example, when in the case of NMR the substance contains immobile nuclei and mobile nuclei, the sampling values (of a quickly exponentially decaying spectroscopic signal) originating from the immobile nuclei can be simply omitted. The sampling values of the tail of an exponentially decaying spectroscopic signal can also be omitted. Thus, convolution effects associated with a transformation to the frequency domain in conjunction with weighting, such as base line (wide background in the spectrum due to quickly decaying signals from the immobile nuclei) and line-shape distortions (due to phase shifts) can be avoided. Fitting is performed partly non-iteratively in order to obtain an initial estimate for at least one of the spectrum parameters used as initial values for further iterative fitting. The non-iterative fitting is comparatively fast and the further iterative fitting enables the method to be used successfully also in the case of a poor signal-to-noise ratio. For parameters which occur linearly in the model function, such as complex amplitudes, no initial values are required, resulting in a faster method. Said article describes the method inter alia for a model function of exponentially damped sinusoids in which parameters such as amplitude, damping factor and frequency occur. Using the least-squares optimisation procedure, the sampling values are iteratively fitted as well as possible to the model function, initial values being required for the damping factor and frequencies which occur as non-linear parameters in the model function. The prior knowledge may comprise a time shift of an instant of a first sample with respect to a time origin and predetermined phases. The least-squares optimisation procedure can be written in the form of a matrix. This is represented by the formula 4 on page 94 of said article, showing a least-squares solution for the amplitude. All terms in the inverse matrix occurring therein are successively calculated, like the terms in the product of the Hermitic matrix with the data vector. In the matrix form a large number of product terms occur, so that a substantial amount of computation time is required for executing the method by means of a computer; this aspect becomes more significant in the case of a comparatively large

number of sampling values.

It is an object of the invention to provide a method which, when the model function contains exponentially damped sinusoids, requires substantially less computation time when executed by means of a computer.

To achieve this, a method in accordance with the invention is characterized in that prior to the iteration the model function is linearised with respect to the spectrum parameters occurring non-linearly, after which inner product terms occurring in the least-squares procedure are converted into an analytic form which is used during iteration. The number of columns of the matrix is increased with respect to the matrix in said article due to residual parameters which remain after linearisation, for example frequency and damping. The invention is based on the idea to convert first the inner product terms into analytic form in order to solve the least-squares problem in the case of exponentially damped sinusoids as the model function, rather than calculate, like in the known method, all matrix products one term after the other for all possible summations by means of row and column multiplications. The computation time is thus substantially reduced. In comparison with the known method, the method in accordance with the invention is 30 times faster in the case of 17 sinusoids and 512 sampling values. Random tests have shown that the Cramér-Rao lower limit for estimating the parameters is at least substantially reached, so that the method produces reliable parameters. The computation time increases in proportion to the first power of the number of sampling values, assuming that the other parameters, for example the number of sinusoids, remain the same.

A version of a method in accordance with the invention is characterized in that terms of the analytic form are recursively determined. Thus, the method can be simply implemented in a computer.

A version of a method in accordance with the invention is characterized in that the model function contains a polynomial whereby the exponentially damped sinusoids are multiplied. A sum of exponentially damped sinusoids does not always constitute a good model function in all circumstances. By multiplication by a polynomial, a model function is obtained which is adapted to circumstances. The inner product terms retain their comparatively simple form.

A version of a method in accordance with the invention is characterized in that the initial estimate of the spectrum parameters occurring non-linearly in the model function is made by means of a non-iterative estimation procedure. Initial values can thus be determined for parameters which occur non-linearly in the model function. For a non-iterative estimation procedure HSVD (Hankel matrix sin-

gular value decomposition) can be used as described in "Improved Algorithm for Noniterative Time-Domain Model Fitting to Exponentially Damped Magnetic Resonance Signals", H. Barkhuijsen et al, Journal of Magnetic Resonance 73, pp. 553-557, 1987.

A preferred version of a method in accordance with the invention is characterized in that the initial estimate of the spectrum parameters occurring non-linearly in the model function is made on the basis of a coarse spectrum obtained from the sampling values by Fourier transformation. In the case of a comparatively poor signal-to-noise ratio, first a filtering operation can be performed. Initial values of the parameters which occur non-linearly in the model function can be determined from the coarse spectrum. These parameters, frequency and damping, can be determined directly from a display screen on which the coarse spectrum is displayed by picking up, using a so-called mouse, at peak locations in the coarse spectrum the peak locations themselves (frequencies) and the peak width at half peak height (a measure of the damping) for supply to the programmed means in a computer. When the coarse spectrum contains excessive phase distortion, first a phase correction method incorporated in the programmed means can be executed, possibly after filtering (in the case of a comparatively poor signal-to-noise ratio), for example as described in an article by C.H.Sotak et al in Journal of Magnetic Resonance, Vol. 57, pp. 453-462, 1984. The phase correction of the coarse spectrum and the determination of the initial values can also be performed by means of a method as described in EP-A 0 316 041, which forms part of the prior art under Art. 54(3) EPC, "Method and device for automatic phase correction of complex NMR spectra", by J. van Vaals.

The invention will be described in detail hereinafter with reference to a drawing, therein

Fig. 1 diagrammatically shows a device in accordance with the invention,

Fig. 2 shows, in the form of a matrix, a set of linear equations in accordance with the invention, to be used for each iteration step during the iteration process,

Fig. 3 shows the analytic form to be substituted, in accordance with the invention, in the set of linear equations given in Fig. 2,

Fig. 4 shows a spectrum obtained by means of the method in accordance with the invention, and

Fig. 5 shows a table containing parameters of the spectrum of Fig. 4.

Fig. 1 diagrammatically shows a device 1 in accordance with the invention. Specifically, a magnetic resonance device for obtaining spectroscopic signals is shown by way of example. The device 1

comprises magnet coils 3 for generating a steady, uniform magnetic field B_0 which are arranged within a shielded space 2. Within the magnet coils 3 there may be arranged a substance. The substance is, for example a body containing solid and liquid components. During operation of the device, the substance being arranged within the magnet coils 3, a slight excess of nuclear spins (of nuclei having a magnetic moment) will be oriented in the same direction as the field B_0. From a macroscopic point of view this is to be considered as a magnetisation M, i.e. an equilibrium magnetisation. The magnet coils 3 may be resistance magnets or superconducting magnets; the device then comprises a d.c. power supply source 4 for powering the magnet coils 3. When the magnet coils 3 are constructed as permanent magnets, the d.c. power supply source 4 will be omitted. The device 1 furthermore comprises means 5 for generating spectroscopic signals, which means include a reference generator 6 for generating a reference signal for supply to an r.f. modulator 7. When activated, the r.f. modulator 7, supplied an r.f. electromagnetic pulse to an r.f. power amplifier 8 which amplifies the r.f. electromagnetic pulse for supply to a transmitter coil 9 which is arranged near the magnet coils 3. When the substance arranged within the magnet coils is irradiated, the equilibrium of the magnetisation M is disturbed and after irradiation there will be generated a magnetic resonance signal when the magnetisation returns to the state of equilibrium, a so-called FID signal (Free Induction Decay). The resonance signal contains spectroscopic information; the signal will be referred to hereinafter as a spectroscopic signal. The device 1 also comprises means 10 for receiving the spectroscopic signals, including a receiver coil 11 for receiving the spectroscopic signals which is connected to a detector 12 for the detection of the modulated spectroscopic signal, for example by quadrature detection. The detector 12, being coupled to the reference generator 6, comprises low-pass filters and analog-to-digital converters as the sampling means for sampling the spectroscopic signals received and detected. The device 1 also comprises control means 13 which serve inter alia for control and timing of the r.f. generator 7. The device furthermore comprises processing means 14 for processing digitised spectroscopic signals 15 (sampling values). The processing means 14 are coupled to the control means 13. The processing means 14 comprise programmed means 16 inter alia for making an initial estimate for at least one spectrum parameter of a spectrum related to the spectroscopic signals in order to perform a least-squares optimisation procedure on the basis of the sampling values. The programmed means 16 furthermore contain a model function of exponentially damped sinusoids,

a non-iterative estimation procedure, iteration means and Fourier transformation means (not shown in detail). The processing means 14 also comprise a RAM memory 17 which is coupled to the programmed means 16. The device 1 furthermore comprises display means 18, inter alia for the display of a spectrum of the spectroscopic signals. A cursor control device 19 is coupled to the display means 18 and the processing means 14. The cursor control device may be a so-called mouse or track ball; as is known, the mouse is formed by a carriage provided with a motion sensor which output signals in response to motion of the mouse. The signals of the motion sensor are applied to the processing means 14 which move a cursor as an indicator across a display screen of the display device in dependence of the signals of the motion sensor. When a given screen position is reached, the screen position can be applied to the processing means by operation of a control member on the mouse. Inter alia for spectroscopy of a part of the substance, so-called volume-selective spectroscopy, the device 1 comprises gradient coils 20 which are controlled by a gradient coil control device 21. The gradient coil control device 21 is controlled by the control means 13. The gradient coils 20 serve to generate field gradients which are superposed on the field B_0. Generally, there can be generated three gradients Gx, Gy and Gz whose field direction coincides with the direction of the steady, uniform magnetic field B_0 and the respective gradient directions of which extend mutually perpendicularly. For a more detailed description of a magnetic resonance device, reference is made to the handbook "Practical NMR Imaging", by M.A. Foster and J.M.S. Hutchinson, IRL Press, 1987, ISBN 1-85221-011-7, Chapter 1, pages 1-48 which describes the general principles of NMR and shows an NMR device. In the case of spectroscopy of the substance or part of the substance, the aim is to obtain information from the substance in the form of a spectrum (in the frequency domain). For NMR, where nuclear spins are excited in the steady field B_0, the relation $\omega = gamma.(1-\sigma).B_0$ holds for excitation of nuclear spins, where ω is a resonant frequency of the nuclear spins, gamma is a gyromagnetic ratio, and σ is a so-called shielding constant of a nucleus. Spin resonance will occur when the resonant frequency is applied. From a macroscopic point of view this implies, vis-a-vis a stationary observer, a precessional motion of the magnetisation M around the field B_0 at the resonant frequency. When the substance contains nuclei having a different σ, the resonant frequency will also be different for these nuclei. This effect is referred to as chemical shift and becomes manifest as different resonant peaks in a spectrum obtained from the resonance signal. In the time domain the

resonance signal can in principle be described as a superposition of exponentially damped sinusoids. The chemical shifts are due to the fact that nuclei effectively experience a different magnetic field due to a different shielding under the influence of the presence of neighbouring electrons. The neighbouring electrons shield the nuclei to a given degree from the field B_0. Thus, chemical components can be identified in a substance by means of NMR spectroscopy. Depending on a selected frequency of the r.f. magnetic pulse, a given spectrum will be obtained. For example, a phosphor spectrum (^{31}P), a carbon spectrum (^{13}C) or a proton spectrum (^{1}H) can be obtained. The surface area below the resonance peaks in the spectrum is directly proportional to the number of nuclei making a contribution for a given frequency. The surface area corresponds to the amplitude in the time domain. In addition to chemical shifts, another interaction also has an effect on the spectrum, the so-called spin-spin coupling, which causes the splitting off of a resonance line which is usually small in comparison with the chemical shift. For a more detailed description of NMR spectroscopy reference is made to pages 249-274 of said handbook by Foster and Hutchinson.

Fig. 2 shows a set of linear equations (2A) to be used in accordance with the invention, for each iteration step during the iteration process. After an initial estimate of at least one spectrum parameter, frequency and damping of peaks occurring in the spectrum in the present example, the parameters frequency and damping and also amplitude are accurately estimated in a number of iteration steps on the basis of the set (2A). Therein, the column vector $\bar{c}$ relates to the amplitudes of the peaks of the spectrum and Re $\bar{c}'$ represents the residual parameters $\Delta\rho$ of the damping ρ and Im $\bar{c}'$ represents the residual parameters Δnu of the frequency nu, M1 to M6 being matrices in the partitioned form of the extended Fisher data matrix M of the least-squares problem, extended with columns for the residual parameters Δ ρ and Δnu for all peaks, and $\bar{v}_1$ to $\bar{v}_3$ a representation of the sampling values. The set (2A) is formed by linearisation of the least-squares problem. The procedure is based on a model function for the magnetic resonance signal x_n of the form:

$$\hat{x}_n = \Sigma_k c_k.\exp[(\rho_k + 2\pi i.nu_k)(n + \delta) + i\phi_k] \quad (1)$$

where $\hat{x}_n$ is a model function of the signal x_n, c_k, nu_k and
ρ_k are parameters of the spectrum of $\hat{x}_n$, being amplitude,
frequency and damping, respectively, for $k = 1, ..., K$, in which K is the number of peaks in the model function. Furthermore, $i = (-1)^{1/2}$. First an initial estimate is made for ρ_k and nu_k. In the working point (ρ_0, nu_0) obtained for the parameters ρ and nu, for each k $\hat{x}_n$ is linearised, producing terms of the form:

$$[c + (n + \delta)\bar{c}'].\exp[(\rho_0 + 2\pi i.nu_0)(n + \delta) + i\phi_0] \quad (2)$$

in $\hat{x}_n.\rho = \rho_0 + \Delta\rho$ and $nu = nu_0 + \Delta nu$. Therein, n represents a
sampling time of the resonance signal, $n = 0, 1, ...,$ N-1 for N sampling operations at instants t_n, δ denotes a time shift caused by instrumental limitations and/or the deliberate omission of sampling values, ϕ_k denotes a phase shift. δ and ϕ_k can be introduced into the model $\hat{x}_n$ as prior knowledge. Furthermore, after linearisation $Re(\bar{c}') = c\Delta\rho$ and $Im(\bar{c}') = 2 \pi c\Delta nu$, which can be simply demonstrated. Formulas (2B) to (2G) follow from further elaboration of the least-squares problem after linearisation. In the formule (2A) to (2G), $\sim$ is a transposition and $*$ is a complex conjugated operation. $f_k(t_n)$ is the kth model function. The information matrix is dimensioned to 3Kx3K. Furthermore:

$$f_k(t_n) = \exp[(\rho_k + 2\pi i.nu_k)(n + \delta) + i\phi_k] \quad (3)$$

After each iteration step the current values of ρ_k and nu_k are replaced, utilising the current values of $\bar{c}_k'$. When $\bar{c}'$ is sufficiently small, the iteration stops. A spectrum is obtained by transforming the model obtained after iteration to the frequency domain, for example by means of the Fourier transformation means. The spectrum can also be calculated directly from the spectrum parameters obtained, using known Lorentz formules, so that any artefacts due to transformation are avoided. The spectrum is displayed by means of the display means 18. The spectrum parameters can also be represented in the form of a table; in that case the Fourier transformation may be omitted. Random tests have demonstrated that the so-called Cramér-Rao lower limit is at least substantially reached. For a further description of the Cramér-Rao lower limit in relation to the Fisher data matrix reference is made to "Handbook of Measurement Science", Vol. 1, P.H. Sydenham, 1982, Wiley, pp. 335-339. For a description of the generally known Fourier transformation means reference is made to the handbook "An Introduction to the Analysis and Processing of Signals" P.A. Lynn, McMillan 1983, pp. 57-64.

Fig. 3 shows the analytic form for the inner product terms to be substituted in the set of linear equations shown in Fig. 2. By elaborating in the formulas (2B) to (2G) the product $f_k(t_n)f_{k'}*(t_n)$, multiplied by a power of t_n, for $f_k(t_n)$ in accordance with (3), terms according to (3A) in Fig. 3 are produced in as far as the part thereof which is dependent on the sampling instant is concerned; therein, 1 in-

dicates the formulas corresponding to the formulas (2B), (2C) and (2D) in Fig. 2. In formula (3A):

$$z = \exp[\rho_k + \rho_{k'} + 2\pi i(nu_k - nu_{k'})] \qquad (4)$$

Formulas (3B) and (3C) show recursive relations for the respective terms corresponding to $l = 0$, 1 and 2. When z approximates 1, an inaccuracy may occur when use is made of the recursive formules (3B) and (3C). By introducing the variable $eps = z - 1$, this problem an be circumvented. (3D) to (3F) show formules for use in such a case. The computation time required will then slightly increase again, notably in the case of a large N, because of the combinations occurring therein, for example when N exceeds $n + 1$. Without substantial loss of accuracy truncation can take place for a suitable value of n, so that the computation efficiency is increased again. For example, in the case of 512 sampling values it will suffice to truncate the summing operations for, for example, $n = 10$.

Fig. 4 shows a spectrum obtained by means of the method in accordance with the invention for in vivo ^{13}C NMR spectroscopy of the liver of a rat. The number of complex sampling operations amounted to 512 with a sampling interval of 50 μs. The frequency scale is given in kHz relative to the irradiation frequency (the chemical shift appears as a spectrum). In Fig. 4 the reference 4A is the cosine FFT (Fast Fourier Transform) of the sampling values (a window is used in order to avoid artefacts), the reference 4B is a spectrum obtained by means of a method other than the method in accordance with the invention, and the reference 4C is the cosine FFT of the model which has been fitted in the time domain by means of the method in accordance with the invention and in which the prior knowledge concerning the phases has been introduced. In accordance with the invention, one operation step required 15 seconds, using the same device, whereas the known method required a period of time which is 30 times longer. The references p1 tp p17 denote resonance peaks. The spectrum shown in Fig. 4C was obtained by means of 8 iteration steps.

Fig. 5 shows a table containing the parameters of the spectrum 4c in Fig. 4. The number of exponentially damped sinusoids was initially set at 25; it was found that 17 sinusoids were of spectroscopic relevance. For each resonance peak there are shown parameters obtained using a method other than the method in accordance with the invention, in this case by means of HSVD without utilising prior knowledge and therebelow the parameters obtained utilising the method in accordance with the invention with introduction of prior knowledge. The errors indicated amount to twice the standard deviation.

Many alternatives are feasible for those skilled in the art without departing from the scope of the invention. For example, in the case of NMR many pulse sequences can be used for spectroscopy in order to obtain resonance signals, both volume selective as well as non-volume selective. For a volume-selective pulse sequence use can be made of the SPARS method, as disclosed in Magnetic Resonance Imaging, Vol. 4, pp.237-239, 1986. Even more prior knowledge can be used, for example information concerning multiplets in the spectrum. For a given signal-to-noise ratio for in vivo NMR, the use of prior knowledge will often be required in order to achieve suitable quantification.

Claims

1. A method of determining spectrum parameters of a spectrum in a frequency domain related to spectroscopic signals in the time domain, in which method the spectroscopic signals derived from a substance are sampled in order to obtain sampling values and are approximated by a complex model function which contains the spectrum parameters and exponentially damped sinusoids, in which method there is also made an initial estimate, based on the sampling values, for the spectrum parameters occurring non-linearly in the model function, the spectrum parameters being accurately estimated from the model function by iteration with a least-squares optimisation procedure, and prior knowledge is introduced into the model function, characterized in that prior to the iteration the model function is linearised with respect to the spectrum parameters occurring non-linearly, after which inner product terms occurring in the least-squares procedure are converted into an analytic form which is used during iteration.

2. A method as claimed in Claim 1, characterized in that terms of the analytic form are recursively determined.

3. A method as claimed in Claim 1 or 2, characterized in that the model function contains a polynomial whereby the exponentially damped sinusoids are multiplied.

4. A method as claimed in Claim 1, 2 or 3, characterized in that the initial estimate of the spectrum parameters occurring non-linearly in the model function is made by means of a non-iterative estimation procedure.

5. A method as claimed in Claim 1, 2 or 3, characterized in that the initial estimate of the

spectrum parameters occurring non-linearly in the model function is made on the basis of a coarse spectrum obtained from the sampling values by Fourier transformation.

6. A device for determining spectrum parameters of a spectrum in a frequency domain related to spectroscopic signals in the time domain, which device comprises means (3, 5), for generating the spectroscopic signals in a substance, sampling means (12) for obtaining sampling values from the spectroscopic signals, and display means (18) for displaying the spectrum, and also comprises programmed means (16) which comprise a complex model function containing the spectrum parameters and exponentially damped sinusoids, and are suitable for storing prior knowledge of the spectroscopic signals as well as for making an initial estimate for the spectrum parameters occurring non-linearly in the model function and for executing a least-squares optimisation procedure for the model function on the basis of the sampling values, the programmed means (16) furthermore comprising iteration means for accurately estimating, using iteration, the spectrum parameters by means of the least-squares optimisation procedure, characterized in that the iteration means contain the model function linearised with respect to the spectrum parameters occurring non-linearly, inner product terms occurring in the least-squares optimisation procedure being present in an analytic form, which analytic form serves for use in the iteration means.

7. A device as claimed in Claim 6, characterized in that the programmed means (16) also contain a non-iterative estimation procedure for making an initial estimate of the spectrum parameters occurring non-linearly in the model function.

8. A device as claimed in Claim 6 which comprises Fourier transformation means, characterized in that the programmed means (16) are also suitable for determining, in conjunction with the Fourier transformation means, a coarse spectrum from the sampling values and for displaying the coarse spectrum by way of the display means (18), the device comprising a cursor control device (19) which is coupled to the display device (18) in order to pick up parameters from the coarse spectrum as an initial estimate for the spectrum parameters occurring non-linearly in the model function.

Patentansprüche

1. Verfahren zum Bestimmen von Spektralparametern eines auf spektralanalytische Signale in der Zeitebene bezogenen Spektrums in einer Frequenzebene, bei dem die von einer Substanz abgeleiteten spektralanalytischen Signale zum Erhalten von Abtastwerten abgetastet und durch eine komplexe Modellfunktion angenähert werden, die die Spektralparameter und exponentiell gedämpfte Sinuskurven enthält, und bei dem außerdem eine anfängliche Schätzung für die nicht-linear in der Modellfunktion auftretenden Spektralparameter auf der Basis der Abtastwerte vorgenommen wird, wobei die Spektralparameter, von der Modellfunktion ausgehend, durch Iteration mit einer Optimierung nach der Methode der kleinsten Quadrate sehr genau geschätzt werden und Vorkenntnisse in die Modellfunktion eingeführt werden, dadurch gekennzeichnet, daß die Modellfunktion vor der Iteration in bezug auf die nicht-linear auftretenden Spektralparameter linearisiert wird und anschließend in der Methode der kleinsten Quadrate auftretende Skalarprodukt-Terme in eine analytische Form umgewandelt werden, die während der Iteration verwendet wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Terme der analytischen Form rekursiv bestimmt werden.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Modellfunktion ein Polynom enthält, mit dem die exponentiell gedämpften Sinuskurven multipliziert werden.

4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß die anfängliche Schätzung der nicht-linear in der Modellfunktion auftretenden Spektralparameter mit Hilfe einer nicht-iterativen Schätzmethode erfolgt.

5. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß die anfängliche Schätzung der nicht-linear in der Modellfunktion auftretenden Spektralparameter auf der Basis eines groben Spektrums durchgeführt wird, das durch Fourier-Transformation aus den Abtastwerten erhalten worden ist.

6. Anordnung zum Bestimmen von Spektralparametern eines auf spektralanalytische Signale in der Zeitebene bezogenen Spektrums in einer Frequenzebene, wobei die Anordnung Mittel (3, 5) zum Erzeugen der spektralanalytischen Signale in einer Substanz, Abtastmittel (12)

zum Erhalten von Abtastwerten aus den spektralanalytischen Signalen, und Anzeigemittel (18) zur Darstellung des Spektrums umfaßt und auch programmierte Mittel (16) enthält, die eine komplexe Modellfunktion mit den Spektralparametern und exponentiell gedämpften Sinuskurven umfassen und sich zum Speichern der Vorkenntnisse über die spektralanalytischen Signale eignen sowie zum Durchführen einer anfänglichen Schätzung für die nicht-linearen Spektralparameter in der Modellfunktion und zum Durchführen einer Optimierung nach der Methode der kleinsten Quadrate für die Modellfunktion auf der Basis der abgetasteten Werte, wobei die programmierten Mittel (16) außerdem Iterationsmittel zum genauen Schätzen der Spektralparameter durch Iteration mit Optimierung nach der Methode der kleinsten Quadrate enthält, dadurch gekennzeichnet, daß die Iterations-Mittel die in bezug auf die nicht-linear auftretenden Spektralparameter linearisierte Modellfunktion enthalten, wobei Skalarprodukt-Terme, die bei der Optimierung nach der Methode der kleinsten Quadrate auftreten, in einer analytischen Form vorliegen, die für die Verwendung in den Iterations-Mitteln dient.

7. Anordnung nach Anspruch 6, dadurch gekennzeichnet, daß die programmierten Mittel (16) auch eine nicht-iterative Schätzungsprozedur für die Durchführung einer anfänglichen Schätzung für die in der Modellfunktion nicht-linear auftretenden Spektralparameter enthalten.

8. Anordnung nach Anspruch 6 mit Fourier-Transformations-Mitteln, dadurch gekennzeichnet, daß die programmierten Mittel (16) sich in Verbindung mit den Fourier-Transformations-Mitteln auch für die Bestimmung eines groben Spektrums aus den Abtastwerten und zur Anzeige des groben Spektrums mit Hilfe der Anzeigemittel (18) eignen, wobei die Anordnung eine Cursor-Steuereinrichtung (19) enthält, die mit der Anzeigeeinrichtung (18) gekoppelt ist, um die Parameter aus dem groben Spektrum als anfängliche Schätzung für die nicht-linear in der Modellfunktion auftretenden Spektralparameter aufzunehmen.

Revendications

1. Procédé pour déterminer les paramètres spectraux d'un spectre (1) dans un domaine de fréquences en relation avec des signaux spectroscopiques (2) dans le domaine temporel, procédé dans lequel les signaux spectroscopiques dérivés d'une substance sont échantillon-

nés aux fins d'obtenir des valeurs d'échantillonnage et sont estimés approximativement par une fonction modèle complexe qui contient les paramètres spectraux et des sinusoïdes amorties exponentiellement, procédé dans lequel est également faite une estimation initiale, basée sur les valeurs d'échantillonnage, pour les paramètres spectraux apparaissant non linéairement dans la fonction modèle, les paramètres spectraux étant estimés avec précision d'après la fonction modèle par itération au moyen d'une procédure d'optimalisation par les moindres carrés, et la connaissance antérieure est introduite dans la fonction modèle, caractérisé en ce qu'avant l'itération, la fonction modèle est linéarisée par rapport aux paramètres spectraux apparaissant non linéairement, après quoi les termes, qui sont des produits internes apparaissant dans l'opération par les moindres carrés, sont convertis en une forme analytique qui est utilisée pendant l'itération.

2. Procédé suivant la revendication 1, caractérisé en ce que les termes de la somme analytique sont déterminés par récurrence.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que la fonction modèle contient un polynôme au moyen duquel les sinusoïdes amorties exponentiellement sont multipliées.

4. Procédé suivant la revendication 1, 2 ou 3, caractérisé en ce que l'estimation initiale des paramètres spectraux apparaissant non linéairement dans la fonction modèle est effectuée au moyen d'une procédure d'estimation non intérative.

5. Procédé suivant la revendication 1, 2 ou 3, caractérisé en ce que l'estimation initiale des paramètres spectraux apparaissant non linéairement dans la fonction modèle est effectuée sur la base d'un spectre grossier obtenu à partir des valeurs d'échantillonnage par transformation de Fourier.

6. Dispositif pour déterminer les paramètres spectraux d'un spectre (1) dans un domaine de fréquences en relation avec des signaux spectroscopiques (2) dans le domaine temporel, lequel dispositif comprend des moyens (3, 5) pour engendrer les signaux spectroscopiques dans une substance, un moyen d'échantillonnage (12) pour obtenir des valeurs d'échantillonnage à partir des signaux spectroscopiques et un moyen d'affichage (18) pour afficher le spectre, et comprend aussi un

moyen programmé (16) qui comprend une fonction modèle complexe contenant les paramètres spectraux et des sinusoïdes amorties exponentiellement et qui convient pour mettre en mémoire la connaissance antérieure des signaux spectroscopiques, de même que pour faire une estimation initiale des paramètres spectraux apparaissant non linéairement dans la fonction modèle et pour exécuter une opération d'optimalisation par les moindres carrés pour la fonction modèle sur la base des valeurs d'échantillonnage, le moyen programmé (16) comprenant, de surcroît, un moyen d'itération pour estimer avec précision, par itération, les paramètres spectraux à l'aide de la procédure d'optimalisation par les moindres carrés, caractérisé en que le moyen d'itération contient la fonction modèle linéarisée par rapport aux paramètres spectraux apparaissant non linéairement, les termes qui sont des produits internes apparaissant dans la procédure d'optimalisation par les moindres carrés étant présents sous une forme analytique, laquelle forme analytique sert dans le moyen d'itération.

7. Dispositif suivant la revendication 6, caractérisé en ce que le moyen programmé (16) contient aussi une procédure d'estimation non itérative pour effectuer une estimation initiale des paramètres spectraux apparaissant linéairement dans la fonction modèle.

8. Dispositif suivant la revendication 6, qui comprend un moyen de transformation de Fourier, caractérisé en ce que le moyen programmé (16) convient aussi pour déterminer, conjointement avec le moyen pour transformation de Fourier, un spectre grossier à partir des valeurs d'échantillonnage et pour afficher le spectre grossier à l'aide du moyen d'affichage (18), le dispositif comprenant a dispositif de commande de curseur (19) qui est couplé au moyen d'affiche (18) afin de collecter les paramètres du spectre grossier en tant qu'estimation initiale des paramètres spectraux apparaissant non linéairement dans la fonction modèle.
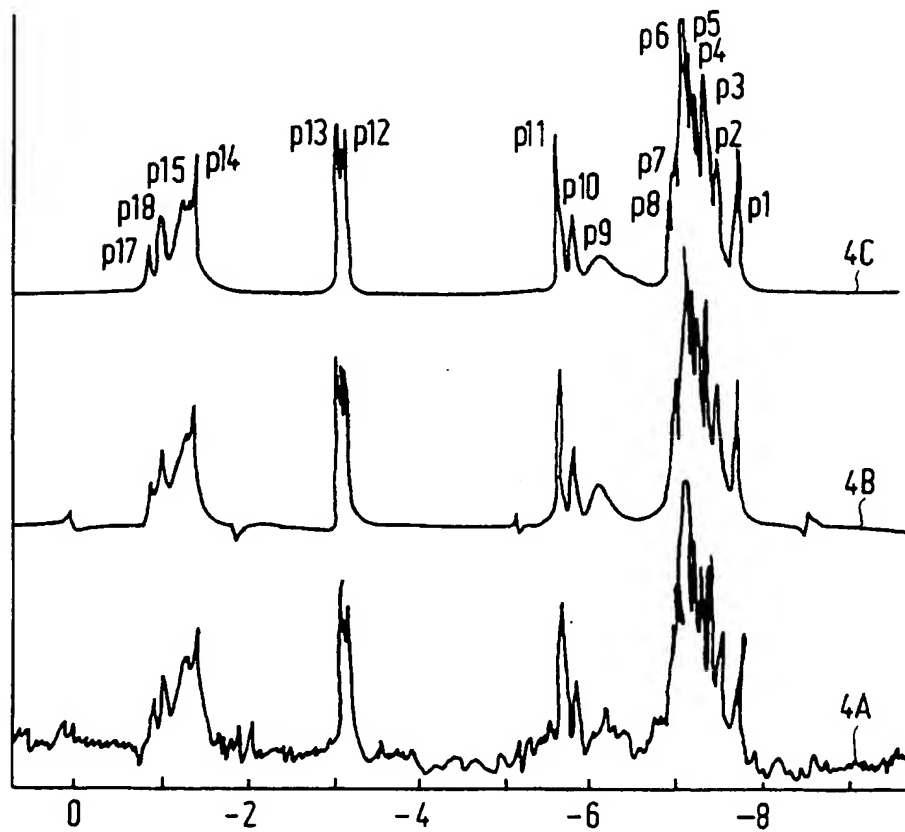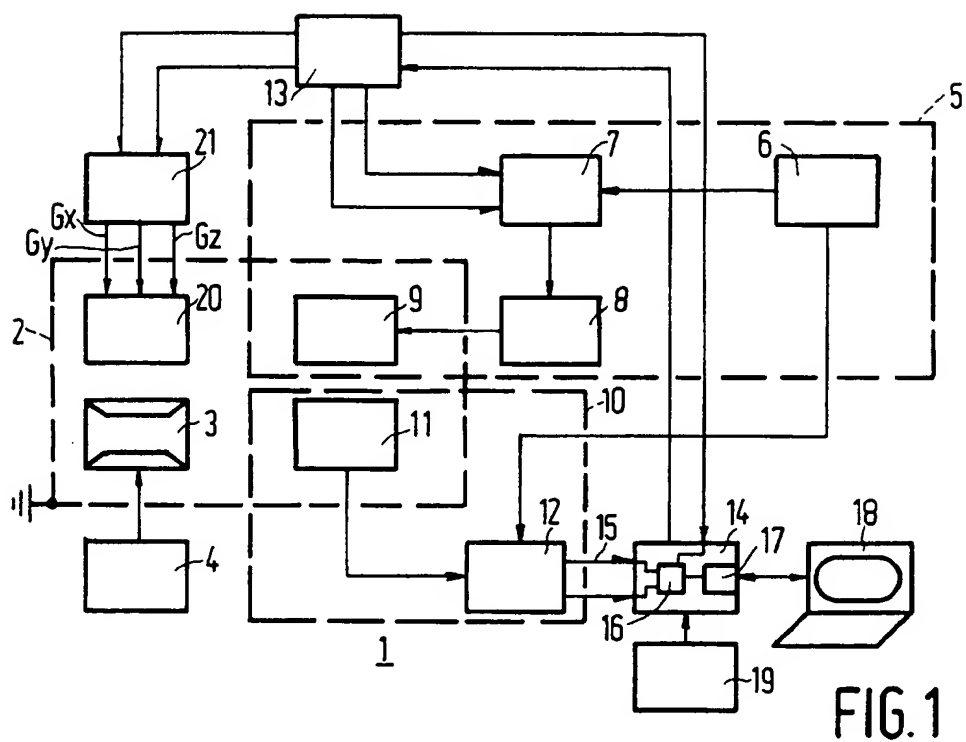
FIG.1

FIG. 4

$$
\begin{bmatrix} \bar{c} \\ \mathrm{Re} \ \bar{c}' \\ \mathrm{Im} \ \bar{c}' \end{bmatrix} = \begin{bmatrix} M_1 & M_2 & M_3 \\ \widetilde{M}_2 & M_4 & M_5 \\ \widetilde{M}_3 & \widetilde{M}_5 & M_6 \end{bmatrix}^{-1} \begin{bmatrix} \bar{v}_1 \\ \bar{v}_2 \\ \bar{v}_3 \end{bmatrix} \tag{2A}
$$

$$
(M_1)_{kk'} = \mathrm{Re} \left[\sum_{n=0}^{N-1} f_k(t_n) \ f_{k'}^*(t_n) \right] \qquad k,k' = 1, \cdots, K \tag{2B}
$$

$$
(M_2 + iM_3)_{kk'} = \sum_{n=0}^{N-1} t_n \ f_k(t_n) \ f_{k'}^*(t_n) \qquad k,k' = 1, \cdots, K \tag{2C}
$$

$$
(M_4 + iM_5)_{kk'} = \sum_{n=0}^{N-1} t_n^2 \ f_k(t_n) \ f_{k'}^*(t_n) \qquad k,k' = 1, \cdots, K \tag{2D}
$$

$$
M_6 = M_4 \tag{2E}
$$

$$
(\bar{v}_1)_k = \mathrm{Re} \left[\sum_{n=0}^{N-1} f_k^*(t_n) \ x_n \right] \qquad k = 1, \cdots, K \tag{2F}
$$

$$
(\bar{v}_2 + i\bar{v}_3)_k = \sum_{n=0}^{N-1} t_n \ f_k^*(t_n) \ x_n \qquad k = 1, \cdots, K \tag{2G}
$$

FIG. 2

$$S_l \quad = \quad \sum_{n=0}^{N-1} n^l \ z^n \qquad\qquad l = 0, 1, 2 \quad (3A)$$

$$S_0 \quad = \quad \frac{1 - z^N}{1 - z} \qquad\qquad (3B)$$

$$S_l \quad = \quad \frac{z \sum_{m=0}^{l-1} \left(\begin{bmatrix} l \\ m \end{bmatrix} S_m \right) - N^l \ z^N}{1-z} \qquad l \geqq 1 \quad (3C)$$

$$S_0 \quad = \quad \sum_{n=0}^{N-1} \begin{bmatrix} N \\ n+1 \end{bmatrix} eps^n \qquad\qquad (3D)$$

$$S_1 \quad = \quad \sum_{n=0}^{N-1} \frac{(n+1) N - 1}{n + 2} \begin{bmatrix} N \\ n+1 \end{bmatrix} eps^n \qquad\qquad (3E)$$

$$S_2 \quad = \quad \sum_{n=0}^{N-1} \frac{(n+1)(n+2) N^2 - 3 (n+1) N - n+1}{(n+2)(n+3)} \begin{bmatrix} N \\ n+1 \end{bmatrix} eps^n \quad (3F)$$

FIG. 3

	v_k	ρ_k	c_k	φ_k
p1	-7.7642 ± 0.0038	-0.074 ± 0.024	$388\pm\ 81$	4 ± 12
	-7.7630 ± 0.0023	-0.082 ± 0.023	$420\pm\ 75$	0
p2	-7.5368 ± 0.0106	-0.193 ± 0.066	650 ± 214	-21 ± 19
	-7.5440 ± 0.0074	-0.335 ± 0.077	1021 ± 178	0
p3	-7.4072 ± 0.0076	-0.173 ± 0.048	1181 ± 417	-24 ± 20
	-7.4142 ± 0.0023	-0.115 ± 0.025	678 ± 118	0
p4	-7.3320 ± 0.0108	-0.203 ± 0.068	1108 ± 475	35 ± 25
	-7.3158 ± 0.0034	-0.170 ± 0.038	820 ± 143	0
p5	-7.2279 ± 0.0041	-0.047 ± 0.026	362 ± 120	-19 ± 19
	-7.2318 ± 0.0018	-0.087 ± 0.020	$596\pm\ 97$	0
p6	-7.1320 ± 0.0014	-0.112 ± 0.009	2983 ± 254	$-14\pm\ 4$
	-7.1365 ± 0.0005	-0.101 ± 0.005	$2556\pm\ 87$	0
p7	-7.0628 ± 0.0084	-0.173 ± 0.053	909 ± 313	56 ± 20
	-7.0397 ± 0.0032	-0.076 ± 0.032	$286\pm\ 78$	0
p8	-6.9742 ± 0.0075	-0.024 ± 0.047	$124\pm\ 80$	29 ± 36
	-6.9690 ± 0.0031	-0.057 ± 0.032	$220\pm\ 68$	0
p9	-6.1432 ± 0.0537	-0.651 ± 0.338	666 ± 264	-8 ± 24
	-6.1743 ± 0.0510	$-1.159\pm.524$	945 ± 524	0
p10	-5.8401 ± 0.0097	-0.120 ± 0.061	285 ± 112	-5 ± 22
	-5.8417 ± 0.0066	-0.127 ± 0.065	259 ± 100	0
p11	-5.6772 ± 0.0039	-0.100 ± 0.025	$538\pm\ 94$	4 ± 10
	-5.6762 ± 0.0021	-0.086 ± 0.020	$482\pm\ 75$	0
p12	-3.1745 ± 0.0047	-0.098 ± 0.030	495 ± 118	-11 ± 13
	-3.1769 ± 0.0028	-0.119 ± 0.027	$585\pm\ 97$	0
p13	-3.1092 ± 0.0036	-0.083 ± 0.023	535 ± 112	-6 ± 12
	-3.1104 ± 0.0018	-0.064 ± 0.019	$430\pm\ 78$	0
p14	-1.4206 ± 0.0097	-0.062 ± 0.061	180 ± 129	-13 ± 41
	-1.4221 ± 0.0040	-0.073 ± 0.050	219 ± 112	0
p15	-1.3540 ± 0.0365	-0.740 ± 0.230	1613 ± 327	15 ± 12
	-1.3075 ± 0.0202	-0.744 ± 0.177	1588 ± 331	0
p16	-1.0660 ± 0.0116	-0.073 ± 0.073	$138\pm\ 93$	2 ± 39
	-1.0639 ± 0.0059	-0.091 ± 0.059	$190\pm\ 86$	0
p17	-0.9049 ± 0.0289	-0.194 ± 0.181	190 ± 140	-56 ± 43
	-0.9256 ± 0.0092	-0.095 ± 0.087	$127\pm\ 78$	0

FIG. 5